CHAPTER 6

XRD CHARACTERIZATION

CHAPTER 6: XRD Characterization for complex formation

6.1 Introduction

In chapter 4, we have shown that there is interaction between chitosan and lithium acetate. In chapter 5 the effect of Al_2O_3 and CeO_2 as dispersoids in enhancing the films' electrical properties has been studied. The film with 2 wt% Al_2O_3 shows the highest value, while with further addition of Al_2O_3, the conductivity decreased. For CeO_2 added samples, there is no significant enhancement in conductivity observed. X-ray diffraction (XRD) technique is then applied to see if there is any changes in the film's crystallinity. It is well known that the nature of the film does affect the electrical conductivity.

The XRD technique can show whether a material is crystalline, amorphous or semi-crystalline. New crystalline peaks might be observed due to the formation of new crystalline phases. In order to analyze the changes in crystallinity, the XRD patterns were taken for samples with different wt% of aluminium oxide and cerium oxide. X-ray diffraction measurements were made for the various complexes to examine the nature of crystallinity with respect to the pure chitosan acetate film.

6.2 X-ray Diffraction Analysis (XRD)

6.2.1 Aluminium oxide

The x-ray diffractogram of chitosan, lithium acetate and aluminium oxide are shown in figure 6.1. The x-ray diffractogram for different wt% of aluminium oxide are shown in figure 6.2. The nature of crystallinity are compared with the pure chitosan, lithium acetate and aluminium oxide in figure 6.1.

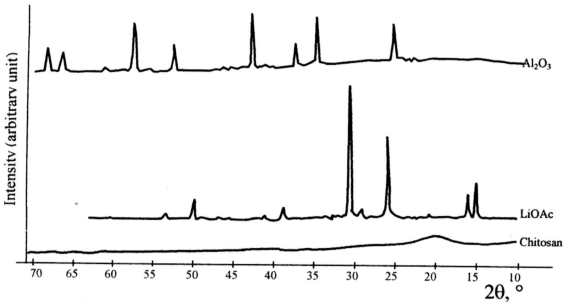

Figure 6.1. X-ray diffractogram of chitosan, lithium acetate and aluminium oxide.

It can be seen that chitosan is an amorphous material where no crystalline peaks are observed. While for lithium acetate salt, five significant peaks are observed. They are at 2θ =15.1°, 16.1°, 25.9°, 30.7° and 50.1°. For aluminium

oxide, more peaks were observed. They are at 2θ = 25.5°, 35.1°, 37.7°, 43.3°, 52.5°, 57.5° and 66.5°.

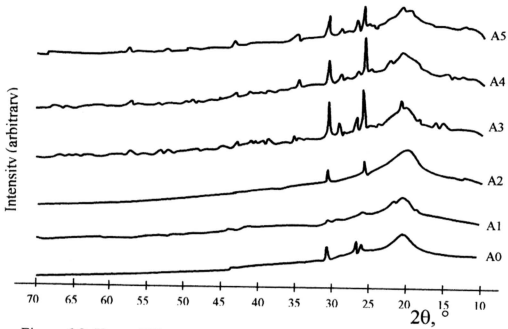

Figure 6.2. X-ray diffractogram for different wt % of aluminium oxide.

Figure 6.2, represents the x-ray diffractograms for samples with and without Al_2O_3. For the films with no Al_2O_3, A0; two LiOAc peaks are observed at 2θ= 25.9° and 30.7°. When 1 wt% of Al_2O_3 is added to the contents of A0, these peaks are diminished to a great extent. This could be due to the slightly lower percentage of LiOAc due to the Al_2O_3 added but it can also imply that Al_2O_3 has disrupted the crystallinity of LiOAc. For sample A2, the increase in Al_2O_3 should reduce the weight percentage of LiOAc but the intensity of the LiOAc peaks have increased. However on the whole the spectrum is smoother compared to A0 and A1. Although A1 seems to be more amorphous than A2, its

room temperature conductivity is lower than sample A2. This could be attributed to less mobile ions in sample A1.

Sample A3 also contains more Al_2O_3 than sample A2 and A1, but the intensity of the LiOAc are even higher than sample A2. If the increase in intensity of the LiOAc represent an increase in the number of Li ions and OAc ions, then the smaller conductivity value of A3 compared to A2 could be attributed to the higher degree of crystallinity of A3. This is because of the presence of Al_2O_3 peaks between $2\theta = 25°$ and 30°.

According to Shahi and Wagner (1982), the enhanced conductivity is usually accompanied by a decrease in activation energy, suggesting that the dispersoids generate excess of lattice defects and thereby increase the conductivity. When more dispersoids are added the aggregate become larger. According to Shahi and Wagner (1992), when more Al_2O_3 particles are dispersed, there is very little or practically no enhancement in conductivity. This is the same as that observed in this work where the magnitude of conductivity of 4 %wt of Al_2O_3 and above is the same as films with no Al_2O_3 added.

In order to quantify the XRD results, the Scherrer equation was used. The degree of crystallinity was determined. Two prominent LiOAc peaks from the XRD patterns have been chosen at $2\theta = 25.9°$ and 30.7° for the linewidth measurements. The measured linewidths and the crystallite size (Scherrer length) calculated for the different sample A0 to A5 are given in table 6.1. It can be seen

that sample A2 has the shortest Sherrer length and therefore it is the least ctystalline compared to A0, A3 ,A4 and A5. A6 and A7 are not compared since they are double layered films.

Table 6.1 shows that the degree of crystallinity decreases when wt% of aluminium oxide increases up to 2 wt% and increase at 3 wt% and 4 wt%. While at 2θ=30.7°, the degree of crstallinity increase for A3 to A4, decrease for A5. The lower degree of crystallinity are shown by A1 and A2 compared to A0.

Table 6.1. Composition, crystallinity data from x-ray diffraction for aluminium oxide as dispersoid. The peaks in A1 are too small that the Scherer length calculation is difficult.

Sample	wt% of aluminium oxide	Crystallinity	
		LiOAc peak 1 at 25.9°	LiOAc peak 2 at 30.7°
A0	0	5.55	5.06
A2	2	4.51	4.07
A3	3	6.70	6.88
A4	4	6.71	7.01
A5	5	6.15	6.62

6.2.2 Cerium oxide

X-ray diffractograms of chitosan, lithium acetate and cerium oxide are shown in figure 6.3, while x-ray diffractogram for different weight % of cerium oxide are shown in figure 6.4. The nature of crystallinity are compared with the pure chitosan, lithium acetate and cerium oxide in figure 6.3.

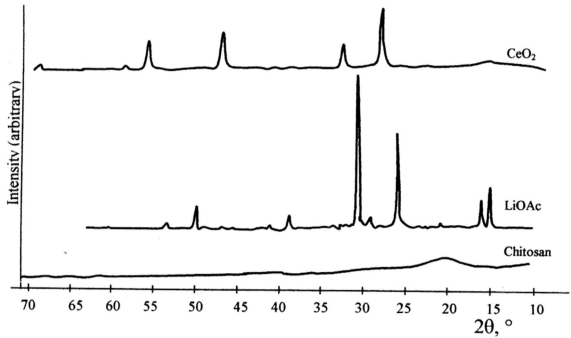

Figure 6.3. X-ray diffractogram of chitosan, lithium acetate and cerium oxide.

The same diffractogram for chitosan and lithium acetate are shown together with the diffractogram for cerium oxide. It can be seen that chitosan is an amorphous material where no crystalline peaks are observed. For the lithium acetate salt, five significant peaks are observed. They are at 2θ =15.1°, 16.1°,

25.9°, 30.7° and 50.1°. For cerium oxide, fewer peaks were observed. They are at 2θ= 28.4°, 32.9°, 47.4° and 56.3°.

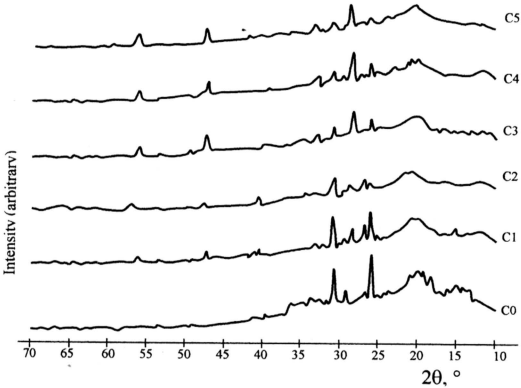

Figure 6.4. X-ray diffractogram for different wt % of cerium oxide.

In figure 6.4, it is observed that there are significant changes in 6 peaks. They are at 2θ=25.9° and 30.7°, which correspondence to LiOAc peaks and at 2θ=28.4°, 32.9°, 47.4° and 56.3°. The changes in these 6 peaks are discussed. For the films with no cerium oxide, we can see the two LiOAc peaks can be

observed. These peaks' intensity decreased with the increase of cerium oxide. While when looking at the other four peaks which correspondence to cerium oxide, it showed the increased in intensities when the concentration of cerium oxide increased. When more cerium oxide is added, the crystallinity due to LiOAc is depressed, however, at the same time, the crystallinity of films due to cerium oxide is increased. This explains why no significant enhancement in electrical properties (conductivity) in chapter 5 is observed.

By using Scherrer equation, the degree of crystallinity was determined. Table 6.2 shows the variation in Scherrer length calculated for the different sample C0 to C5.

Table 6.2. Composition, crystallinity data from x-ray diffraction for cerium oxide as dispersoid

Sample	wt% of cerium oxide	Crystallinity (peak at different 2θ)					
		25.9°	30.7°	28.4°	32.9°	47.4°	56.3°
C0	0	5.67	5.38	4.30	-	-	-
C1	1	5.06	4.03	4.50	-	-	-
C2	2	4.21	4.06	-	-	-	-
C3	3	3.86	4.04	3.94	6.52	4.76	5.80
C4	4	-	3.89	3.94	3.85	4.36	5.44
C5	5	-	3.05	4.79	6.67	5.87	6.27

From table 6.2, the degree of crystallinity decreases when the concentration of cerium oxide increases up to 3 wt%. The 25.9° peak disappeared with 4 wt% cerium oxide and above. While at 2θ=30.7°, the crystallinity does not exhibit significant changes with increase concentration of cerium oxide. The same characteristics are shown for 2θ=32.9°, 47.4° and 56.3° which correspondence to cerium oxide peaks. C2 exhibits the least degree of crystallinity. C6 and C7 are not discussed since they are double layered films.

6.3 Summary

From XRD analysis, it is found that the least crystallinity is exhibited by the sample A2. This corresponds to the higher conductivity exhibited by this film. For cerium oxides complexes, the high crystallinity nature causes the low conductivity exhibited by these films.